Other Tire-Derived Chemicals of Interest

SUMMARY AND QUESTIONS FOR JULY 2021 DTSC WORKSHOP

The California Department of Toxic Substances Control's (DTSC) Safer Consumer Products Program has added Motor Vehicle Tires as a new product category in its 2021-2023 Priority Product Work Plan. DTSC has conducted a preliminary screening of chemicals presumed to be found in tires that may be of concern for the aquatic environment. This is part of an initial evaluation of this category, in conjunction with ongoing work on zinc and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) in motor vehicle tires. To advance our work on tires, DTSC is seeking information related to the chemicals highlighted in this document and, specifically, the related questions. DTSC also welcomes information on other chemicals in tires that may be of concern for the aquatic environment.

CHEMICALS: BENZOTHIAZOLES

Overview

Benzothiazoles and 2-mercaptobenzothiazole (CASRN 149-30-4) are a class of chemicals used in tires as vulcanization accelerators during the manufacturing process.[1] Many benzothiazole derivatives can be found in finished tires.[2] In some cases, benzothiazole derivatives are considered impurities and have been used as an indicator of tire wear particles in the environment.[2,3] Benzothiazoles are known to leach from tires.[4–6] While the data are limited, these compounds have been found in stormwater runoff and road dust in California and in sediments in San Francisco Bay.[7,8]

2-mercaptobenzothiazole is the only benzothiazole on DTSC's Candidate Chemicals List and may cause cancer. 2-mercaptobenzothiazole has also been found to be environmentally persistent and to impair wildlife survival. These hazard traits may also apply to others in the larger class of benzothiazoles.[9–13]

Questions

- Are benzothiazoles used in all tires? If not, what determines what applications they are used in?
- Which benzothiazoles are used in tires and at what concentrations? How does this vary across tire types or brands?
- What is the function of benzothiazoles in tires? What determines which benzothiazoles are used in a tire?

- Please provide information on the benzothiazole impurities that have been identified in the benzothiazole source material used in tires, such as 2-(4-morpholinyl)benzothiazole and N-cyclohexyl-2-benzothiazolamine, and whether these benzothiazole impurities have also been identified in tire products.
    - If they have been, at what concentrations?
    - How are these impurities formed?
    - Are impurities present in the original benzothiazole material used, or created during vulcanization?
- What techniques, if any, are used to remove benzothiazole derivatives that are present in tires as impurities?
- Have there been evaluations of safer alternatives for benzothiazoles used in tires? If yes, which alternatives were identified and what data were used for the evaluation?

CHEMICALS: CHLORINATED PARAFFINS

Overview

Chlorinated paraffins (CPs) are a group of hydrocarbons of various chain lengths in which multiple hydrogen atoms are substituted with chlorine atoms; they can be divided into short- (SCCP; ≤C10-13), medium- (MCCP; C13-17), and long-chained (LCCP; ≥C18) congeners.[14] CPs are included as a class in DTSC's Candidate Chemicals List. SCCPs are no longer produced in the United States and have presumably been replaced with MCCPs and LCCPs.[15] CPs have been detected worldwide, in almost every environmental compartment and in remote areas.[15]

CPs perform a variety functions in manufacturing processes and repair of tires (or other rubber parts), and for general vehicle repair and maintenance, including use as lubricants and rubber additives.[15–21] CPs have been identified in crumb rubber.[14]

CPs as a class are considered to be bioaccumulative and persistent.[18] Within the class of CPs, as chain length and degree of chlorination increases, the likelihood of bioaccumulation and persistence increases.[18] Individual CPs, some of which have also been identified in tire manufacturing, have been shown to be toxic to aquatic species such as invertebrates.[18,22–26]

Data on the presence of CPs in the aquatic environment in North America are limited.[27,28] A 2008 study conducted by the San Francisco Estuary Institute identified SCCPs in white croaker, cormorant eggs, and harbor seal blubber collected from San Francisco Bay.[28] Indirect data are available for leaching of CPs from the rubber components within kitchen blenders,[29] but not specifically from tires. At this time, more data are needed to understand if tires are a source of CPs to the environment.

Questions

- Which CPs are used in tires and at what concentrations?
- What is the function of CPs in tires? What determines which CPs are used in a tire?
- Are CPs used in all tires? If not, what determines which applications they are used in?
- Could you provide data on CP degradation, leachability, or reaction byproducts in tires?
- Have there been evaluations of safer alternatives to CPs used in tires? If yes, which alternatives were identified and what data were used for the evaluation?

CHEMICAL: 1,3-DIPHENYLGUANIDINE

Overview

1,3-diphenylguanidine (DPG), CASRN 102-06-7, is currently not on DTSC's Candidate Chemicals list. DPG is used industrially as a rubber component, accelerator, fuel additive, process regulator, and process aid.[30] In tires specifically, DPG is used to accelerate the vulcanization process during manufacturing.[31,32]

DPG has been detected in the aquatic environment, specifically in roadway runoff and waters affected by urban runoff in California.[33,34] A study by Peter et al.[32] also found DPG in road runoff and surface water in the Seattle, Washington area, further confirming the presence of DPG in the environment. In addition, DPG has been shown to leach from tires, indicating that tires may be a source of DPG in the aquatic environment.[35]

DPG is a registered substance under the European Chemicals Agency REACH regulation, where it is classified as toxic to aquatic organisms, with a potential to cause long-term adverse effects in the aquatic environment.[36] Specifically, DPG is considered toxic to fish, aquatic invertebrates, and algae, and is not readily biodegradable (ECHA 2021). DPG is also classified as a persistent, mobile, and toxic (PMT) substance and as a very persistent, very mobile (vPvM) substance, under criteria developed by the German Environment Agency.[37]

Questions

- Is DPG used in all tires? If not, what determines what applications it is used in?
- What is the typical concentration of DPG used in tires? How does this vary across tire types or brands?
- What factors influence the leachability of DPG from tires? What information is available on the rate and extent of leaching of DPG from tires to the environment?
- Can you provide additional toxicology or monitoring data for DPG that we should be aware of?
- Have there been evaluations of safer alternatives for DPG in tires? If yes, which alternatives were identified and what data were used for the evaluation?

CHEMICALS: (METHOXYMETHYL) MELAMINES

Overview

Methoxymethyl melamines are a family of related chemical compounds characterized by a 1,3,5-triazine ring. There are no methoxymethyl melamines on DTSC's Candidate Chemicals List. Hexamethoxy methylmelamine (HMMM), CASRN 3089-11-0, appears to be the methyoxymethyl melamine with the most widespread industrial use.

HMMM has been generically described as a “cross-linker”; it is used in certain fabric, textile, and leather products, paints, coatings, some plastic and rubber products, and glazing and polishing agents, as well as tires.[38–43] DTSC was unable to find any specific information regarding the function or quantity of HMMM used in tires.

Methyoxymethyl melamines have been identified in road runoff, urban creeks, and leachate from tire wear in the state of Washington.[32] While additional data on the presence of methoxymethyl melamines in the aquatic environment are lacking, it appears that HMMM from road runoff may be a ubiquitous contaminant of urban watersheds.[44] Toxicity and hazard information for HMMM and other methoxymethyl melamines is exceedingly limited. There have been some reports that HMMM is toxic to daphnia, commonly called water fleas, which are important components of many aquatic food chains, but aquatic toxicity has generally been considered low.[45] However, the potential toxicity of HMMM has not been fully evaluated.[45]

Questions

- Are methoxymethyl melamines used in all tires? If not, what determines what applications they are used in?
- Which methoxymethyl melamines, including HMMM, are used in tires and at what concentrations? How does this vary across tire types or brands?
- What is the function of methoxymethyl melamines in tires? What determines which methoxymethyl melamines are used in a tire?
- Could you provide additional toxicology or monitoring data for methoxymethyl melamines that we should be aware of?
- Have tire manufacturers evaluated alternatives to the use of methoxymethyl melamines in tires? If yes, which alternatives were identified and what data were used for the evaluation?

CHEMICALS: OCTYLPHENOL ETHOXYLATES

Overview

Octylphenol ethoxylates (OPEs) are a subclass of alkylphenol ethoxylates that range in degree of ethoxylation. The entire class of OPEs is on DTSC's Candidate Chemicals List. Since OPEs degrade into octylphenol (OP), we have also included OP in our review of this class. These chemicals are typically used as surfactants[46,47] and are used in a number of automotive-related applications, including automotive maintenance and repair and in general automotive consumer care products such as tire cleaning products, automotive paint, automotive lubricants, and anticorrosive materials and paints.[48,49] OP and OPEs have been detected in rubber products.[48–50] OP is most likely present as an impurity due to its use as an intermediate for producing phenolic resins that are used in vulcanization during the tire manufacturing process.[50] At this time, it is unknown whether OPEs in rubber degrade to OP within the tire itself.

In the aquatic environment, OPEs degrade to less ethoxylated OPEs species or to OP.[51] OP and OPEs have been found to have the following hazard traits: endocrine toxicity, bioaccumulation, environmental persistence, and wildlife impairment (survival, reproduction, and possibly development).[52–57] General trends for alkylphenol ethoxylates indicate increasing toxicity with decreasing degrees of ethoxylation.[53] Thus, OPEs become increasingly toxic as they break down in the environment.

OP and OPEs have been detected in the aquatic environment,[32,58–62] which has been typically attributed to their use as surfactants. There is currently no clear evidence that these chemicals leach from tire rubber into the environment. More information is needed to better understand the potential for tires to contribute to aquatic organisms' exposure to OPEs and OP.

Questions

- Are OP/OPEs used in all tires? If not, what determines the applications they are used in?
- Which OP/OPEs are used in tires and at what concentrations? How does this vary across tire types or brands?
- What is the function of OP/OPEs in tires? What determines which OP/OPEs are used in a tire?
- What techniques, if any, are used to reduce the OP and OPEs present in tires as impurities?
- What data are available on the degradation of OPEs to OPs during manufacturing?
- What factors influence the leachability of OP/OPEs from tires? What information is available on the rate and extent of leaching of OP/OPEs from tires into the environment? What information is available on the contribution of tires to the levels of OP and OPEs measured in the environment?
- Have there been evaluations of safer alternatives for OP/OPEs in tires? If yes, which alternatives were identified and what data were used for the evaluation?

CHEMICALS: POLYCYCLIC AROMATIC HYDROCARBONS

Overview

Polycyclic aromatic hydrocarbons (PAHs) are a class of over a hundred different compounds consisting of molecules with two or more fused benzene rings.[63,64] The entire class is included on DTSC's Candidate Chemicals List. PAHs occur naturally as complex mixtures in materials such as crude oil and gasoline, or can be formed during incomplete combustion of fossil fuels, wood, garbage, and other organic matters.[63,64] PAHs can also be manufactured as single compounds.[63] PAHs can be found in tires from their use as extender oils,[2] which are used to improve rubber properties and processing and in reinforcing agents such as carbon black.[65]

PAHs are found ubiquitously in California, including in stormwater runoff,[66] sediments,[67,68] surface water,[68,69] and aquatic organisms.[68] Although structurally diverse, PAHs share similar chemical properties and mechanisms of toxicity; they are often represented by benzo[a]pyrene, a well-studied PAH that is among the class members found in tires. Benzo[a]pyrene is classified by the European Chemicals Agency's REACH legislation as a candidate substance of very high concern because it is a carcinogenic, mutagenic, and reproductive (CMR) toxicant that is persistent, bioaccumulative, and toxic (PBT) and very persistent and very bioaccumulative (vPvB).[70] Benzo[a]pyrene and other PAHs are very toxic to aquatic life at multiple trophic levels, including fish, invertebrates, and algae and have long lasting effects.[70,71] They can impair wildlife survival, development, and reproduction.[70,71]

Questions

- Are there any industry standards regarding which PAHs can be used in tires manufactured or sold in the United States, and at what concentrations?
- Are highly aromatic oils still used as extender oils in tires sold in the United States?
- What concentration of PAHs are found in carbon black used in tires sold in the United States? What data are available on the likelihood of PAHs from carbon black used in tires being released to the aquatic environment?
- Do other components of tires beyond extender oils and carbon black contain PAHs? If so, at what concentrations?
- Have there been evaluations of safer alternatives for PAHs in tires? If yes, which alternatives were identified and what data were used for the evaluation?
- Can you provide aquatic toxicity data for PAHs from carbon black?
- Why are alkylated PAHs used in tires? How does their use in tires differ from non-alkylated PAHs? What are the concentrations of alkylated PAHs in tires and in which tire components?

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